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TESTING AND EVALUATION OF POTENTIAL HAZARDS FROM A TEFLON IMPRE--ETC(U)

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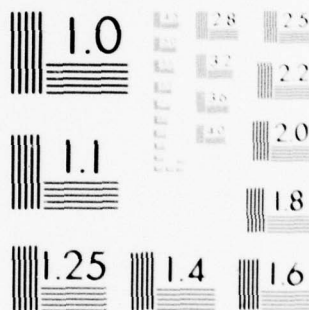
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Testing and Evaluation of Potential Hazards from a Teflon Impregnated Packing

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20. Abstract (Continued)

contaminants outgassing from the packing material as a function of temperature.

→ Under normal operating conditions, no significant amounts of hydrocarbons, fluorides, perfluorocarbons, and asbestos were discharged into the atmosphere or the lubricating, water stream. A trace amount of fluoride ion detected in the water samples can be attributed to a polyfluorinated surfactant identified during the g.c. - mass spectroscopic analysis.

Under severe or "dry" operating conditions, some hydrocarbons, HF, fluorocarbons, and asbestos are discharged into the atmosphere. The observed hydrocarbons are easily absorbed by the charcoal filters, readily oxidized to $\text{CO}_2/\text{H}_2\text{O}$ by the catalytic burners, and should be essentially removed from the machinery space in 30 minutes with normal air exchange. However, the hydrocarbon concentration may reach 400 ppm in the vicinity of the pump, and the hydrocarbons have a characteristic unpleasant odor.

The concentration of asbestos, HF, perfluorocyclopropane, and perfluoroethylene released under the conditions of the test and expanded into the machinery space of SSN 688 are below the currently established NIOSH standards.

The most toxic decomposition product of Teflon, perfluoroisobutylene, can be produced in dangerous quantities only with simultaneous failure of the water lubricating system, the air handling system and with manual tightening of the packing. The likelihood of the triple failure occurring was assessed to be negligible. ↙

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TESTING AND EVALUATION OF POTENTIAL HAZARDS FROM A TEFLON IMPREGNATED PACKING

I. INTRODUCTION

A Teflon impregnated packing is being considered as a replacement for packings currently used on submarine's main and other water pumps. Produced under Military Specification MIL-P-24377 (Ships), the proposed packing material consists of chrysotile asbestos yarn with reinforcing fibers that are impregnated with virgin PTFE (polytetrafluoroethylene), and surface coated with refined white petrolatum. Under normal operating conditions the packing is lubricated with a small stream of water. However, during pump startup, or either as a result of pump failure or operator error, the possibility exists of operation with a "dry" packing. During "dry" operating conditions, the petrolatum and Teflon may thermally decompose and evolve toxic gases which would enter the enclosed atmosphere of the submarine. In addition, asbestos fibers may be released into the atmosphere and the lubricating water stream at a level which could be hazardous to personnel. The Naval Research Laboratory (reference (1)) was tasked to evaluate the potential environmental hazard under the most severe conditions as well as more typical operating conditions.

II. REACTIVITY OF PACKING MATERIALS

Petroleum products can be cracked at temperatures exceeding 400°C to produce lighter hydrocarbons (reference (2)). However, at lower temperatures (<200°C), the low boiling petrolatum coating on the packing will begin to vaporize and decomposition of the less stable hydrocarbons may initiate. The specific hydrocarbon gases

Note: Manuscript submitted May 2, 1979.

evolved from the packing depend upon the petrolatum chemical composition and the reaction conditions; in general, however, hydrocarbons in the petrolatum are relatively nontoxic.

Teflon (PTFE) will decompose at elevated temperatures ($>400^{\circ}\text{C}$) by a reverse mechanism of the polymerization to form perfluoroethylene (PFE) (reference (3)). Perfluoroethylene can then react with oxygen and water in the atmosphere to produce carbonyl fluoride and hydrogen fluoride. At temperatures $>500^{\circ}\text{C}$, PTFE will decompose to perfluorocyclopropane (PFCP) and perfluoroisobutylene (PFIB) in addition to perfluoroethylene. The degree of toxicity (reference (3), (4)) of these decomposition products is given below:

	Approximate lethal concentration (4-hour exposure)
perfluoroethylene	40,000 ppm
perfluorocyclopropane	non-toxic
perfluoroisobutylene	0.5 ppm
hydrogen fluoride	200 ppm (Threshold Limit Value 3.0 PPM)

III. PACKING TESTS CONDUCTED AT DAYTON T. BROWN, INC.

A report (reference (5)) outlines the packing tests conducted at Dayton T. Brown, Inc. which simulated both severe and normal shipboard operations. The test stand and packing housing were constructed so that one set of packing would be tested at a time and in a manner to simulate a SSN 688 class ships' main feed pump stuffing box (see figures 1,2).

The shaft sleeve, shaft sleeve nut, packing gland, and packing were actually SSN 688 class ship's main feed pump parts, purchased new for use in these tests. Packing temperature was monitored continually at three locations: the innermost ring, the center, and the outermost packing ring. Air and water leakage rates across the packing were measured with a flowmeter and a graduated cylinder, respectively. Figures 3-6 depict the test stand and detail the interior of the stuffing box with packing and packing gland in place.

For each test, the shaft was brought up to the designated speed and the packing gland tightened until the desired leakage rate was achieved. During the course of each test, the packing gland was readjusted, when necessary, to maintain the desired leakage rate. Each test ran for 2 hours or until the packing failed, whichever occurred first.

Severe operating conditions were simulated by running the packing without a lubricating water stream ("dry") while injecting air at 50 psig and 60°F into the rear of the stuffing box. The tests were carried out at shaft speeds of 3600, 1800, and 600 RPM with zero or 2 liters/minutes of air leakage past the packing. Air leaking past the packing was continually monitored for toxic materials and concentrated for subsequent laboratory trace analysis at NRL.

During zero leakage tests, the packing would occasionally seize the pump shaft, resulting in very high peak packing

temperature. However, this action was immediately followed by high air leakage rates and subsequent cooling of the packing. As a result, the peak temperatures were held for only a few seconds. Elevated packing temperatures could be maintained only by constant manual adjustment of the packing.

The packing shown in Figure 7 is typical of those used in severe operation testing. As can be seen, the interior surface of the packing has been badly burned and all that remains is the asbestos yarn. The petrolatum was vaporized or decomposed, and the bulk of the Teflon probably removed as fine particulates. The accumulation of waxy dust in the stuffing box is shown in Figure 8.

Simulation of more typical conditions consisted of injecting water at 160°F and 100 psig into the rear of the stuffing box. As was the case for the air tests, the shaft was operated at 3600, 1800, and 600 RPM under zero leakage and 8-16 drops/minute leakage rates. At the completion of each test run, water samples were collected by NRL for subsequent fluoride ion and asbestos content analysis.

Packing used in the "wet" zero leak tests had to be constantly adjusted to maintain zero leakage. In addition, moderate peak packing temperatures were observed. As a result, some scorching of the packing took place. A typical packing is shown in Figure 9. Damage to the packing material was much less severe than that experienced in the air tests.

Tests with water leakage rates of 8-16 drops/minutes gave more favorable results. Leakage rates were relatively easy to maintain and the problems with high packing temperatures and scorching did not occur. The test conditions produced negligible damage to the packing material (Figure 10).

IV. SAMPLING AND ANALYSIS DURING DRY OPERATION

The sampling configuration is shown in Figure (1). Particulates in the gas sample stream were collected on a 0.8μ polycarbonate filter while gaseous hydrocarbons and Teflon decomposition products were monitored with a Wilks Model 80 Infrared Analyzer. Lithium hydroxide traps were used to collect hydrogen fluoride in the gas stream. The flow rate through the sample system was held at two liters per minute by a critical orifice incorporated in the sampling pump.

During dry test operations, the major portion of the material outgassing from the packing consisted of gaseous hydrocarbons and condensed hydrocarbons in the form of an aerosol cloud. After approximately five-ten minutes of operation, the amount of outgassing hydrocarbons dropped significantly. Unfortunately, the level of hydrocarbons was still high enough to prevent on-site detection of low levels of Teflon decomposition products.

Hydrogen fluoride collected on the lithium hydroxide traps was removed using standard analytical procedures and measured

with a fluoride specific electrode. Blank samples of the distilled water used in this analysis and in the "wet" runs gave a fluoride ion background of 0.64 ppm/gal. The small amount of HF detected in the lithium hydroxide traps (Table 1) can be attributed to hydrolysis of a polyfluorinated surfactant (see Section VII), since Teflon does not decompose until it reaches 450°C. Under the most severe conditions of prolonged "dry" operation (high shaft RPM's coupled with a lack of compartment air exchange), the highest HF concentration in the machinery space of a 688 class boat should not exceed 1 PPM. The current TLV for HF is 3 PPM (reference (4)).

Particulate samples collected on the polycarbonate filter were analyzed for asbestos content by electron microscopy. The measured atmospheric asbestos levels resulting from the packing material (Table 2) were well below the current accepted NIOSH standards (reference (6)).

V. SAMPLING AND ANALYSIS DURING WET OPERATION

The test stand and water circulation system used to simulate normal operating conditions is outlined in Figure 2. Water samples were taken from the circulation system at the conclusion of each test run and analyzed at NRL for asbestos fiber and HF concentration. Particulates were filtered from the water samples and burned in a muffle furnace leaving only the asbestos fibers which were examined under polarized light with an optical microscope. The asbestos content of the water was found to be too low

to be accurately measured (Table 2). Hydrogen fluoride contamination of the water sample was measured with a fluoride specific electrode and found to be insignificant (Table 3). As in the case of the air samples, the detected HF can be attributed to hydrolysis of the fluorocarbon surfactant. No hydrocarbons, asbestos, or perfluorocarbons were observed to be released into the atmosphere.

VI. TEMPERATURE ANALYSIS DURING TEST OPERATIONS

Packing temperature near the shaft was continually monitored during the simulation tests. During dry operation, packing temperature averaged 200-315°C (400-600°F) with peak temperatures of ~480°C (900°F). Packing temperatures during wet operation averaged 99-104°C (210-220°F) and never exceeded ~144°C (300°F). Peak temperatures were reached for a period of less than 30 seconds in tests ranging from 10-120 minutes. The observed packing temperatures are summarized in Table (4).

VII. IDENTIFICATION OF VAPOR PHASE PRODUCTS

Identification of the packing outgassing products was carried out at NRL. Sections of packing and stainless steel chips were heated in a closed quartz tube to the temperatures observed in test runs conducted at Dayton T. Brown, Inc. Gas samples were taken at the typical packing temperatures and analyzed by g.c.-mass spectroscopic techniques. The composition of the gas sample was found to be dependent upon heating time, temperature, and the presence of catalytic surfaces (stainless steel). In general, heating of the packing at 130°C

(266°F) produced a small amount of a straight chain fluorocarbon (Figure 11), while packing temperatures of ~200-300°C (392-572°F) produced gas mixtures consisting of branched and straight chain paraffins, acetaldehyde, methyl furans, carbon monoxide, and other partially oxidized hydrocarbons (Figure 12). The straight chain fluorocarbon is thought to serve as a surfactant in the packing manufacturing process. Teflon decomposition products were observed, via infrared spectroscopy, only when packing temperature reached 450-600°C (842-1112°F). Table 5 summarizes the observed composition of the outgassing products as a function of temperature.

VIII. CONCLUSIONS

Tests at Dayton T. Brown, Inc., subsequent laboratory analysis of the air and water samples, and laboratory characterization of the proposed packing allow several conclusions to be made.

Significant amounts of hydrocarbons, fluorides, perfluorocarbons, and asbestos, are not discharged into the atmosphere or bilge when the proposed packing is used under normal, "wet", operating conditions. The slow rate of HF production will result in less than 0.01 gram of HF being added to the bilge in 90 days of continuous operation. In addition, HF production is caused by hydrolysis of the polyfluorinated surfactant, not Teflon decomposition. Furthermore, the trace amount of asbestos discharged into the bilge is coated with petrolatum which will

inhibit release of the fibers into the atmosphere.

Varying amounts of hydrocarbons, HF, fluorocarbons, and asbestos are discharged into the atmosphere when the proposed packing is used under abnormal or "dry" conditions.

The hydrocarbons released into the atmosphere during "dry" operation come from the petrolatum on the packing. After approximately 10 minutes of operation, all the petrolatum at the packing shaft interface is gone, and the atmospheric hydrocarbon concentration in the vicinity of the pump may reach as high as 400 ppm (based on C_6). This exceeds the BUMED 90 day exposure limit for total hydrocarbons (reference (7)), although a one hour exposure limit has not been established. The observed hydrocarbons are easily absorbed by the charcoal filters and readily oxidized to CO_2/H_2O by the catalytic burners. These hydrocarbons have, however, a characteristic, unpleasant odor. As graphically illustrated in Figure 13, the hydrocarbons should be essentially removed from the machinery space in 30 minutes. The hydrocarbon concentration was estimated by assuming dry operation, normal compartment air exchange, and dispersion of the hydrocarbons throughout the volume of the machinery space.

The concentrations of HF and asbestos released under the conditions of the test and expanded into the machinery space of an SSN 688 class boat are below the currently accepted NIOSH standards (references (4) and (6)). After thirty minutes of continuous "dry" operation and no compartment air exchange, the concentration of

perfluoroethylene and perfluorocyclopropane in the machinery space will be less than 1 ppm. There are no currently accepted exposure levels for perfluoroethylene and perfluorocyclopropane, however, the ALC (approximate lethal concentration, 4 hour exposure) is 40,000 ppm for perfluoroethylene (reference (3)) and perfluoroalkanes such as perfluorocyclopropane exhibit very low toxicity (reference (3)).

The most toxic decomposition product of Teflon, perfluoroisobutylene (PFIB), requires special attention since an exposure to 0.5 ppm for four hours can be fatal (reference (3)). PFIB was observed in the laboratory tests only when the packing temperature exceeded 900°F, and was not observed during on site testing at Dayton T. Brown, Inc. when the packing reached 900°F for approximately 30 seconds in 30 minutes of dry operation. Based on the temperature measurements obtained during tests at Dayton T. Brown, prolonged "dry" operation at high shaft speeds would be needed to produce the temperature required to generate PFIB. Three failures are required to produce the conditions necessary for production of dangerous levels of PFIB. Failure of the water lubricating system and the air handling system would have to occur, and the packing would have to be manually tightened, simultaneously, during "dry" operation. The likelihood of the triple failure occurring was assessed to be negligible (reference (8)). Momentary "dry" operation does not generate the packing temperature necessary to produce dangerous levels of PFIB.

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Table 1

Dry Operation HF Conc - Air Run

<u>Test #</u>	<u>RPM</u>	Estimate of	<u>Run Time</u>
		HF Conc in Machinery Air Space (No exchange or Loss) \pm 50%	
1 (Garlock)	3600	.01 PPM	10 minutes
1A (John Crane)	3600	.5	40 minutes
2 (Garlock)	1800	1.5	88 minutes
3 (John Crane)	600	.01	25 minutes
7 (Garlock)	3600	1.0	13 minutes
8 (Garlock)	1800	0.5	76 minutes
9 (Garlock)	600	0.5	120 minutes

Table 2

Measured Asbestos

	<u>Observation</u>
Wet Operation	Trace in Water*
Dry Operation	Trace*

* $<1000/M^3$

Table 3

HF Conc. - Water Run (Normal Conditions)

<u>Test #</u>	<u>RPM</u>	<u>Grams [HF]/Min in Water</u>	<u>Run Time</u>
4 (Garlock)	3600	5×10^{-7}	94 minutes
5 (John Crane)	1800	4×10^{-7}	120 minutes
10 (Garlock)	3600	4×10^{-7}	120 minutes
12 (Garlock)	600	2×10^{-7}	120 minutes

Table 4

Measured Temperatures During Simulation Tests

Dry Operation - Average - 400-600°F (200-315°C)

Peak - ~900°F (480°C)

Wet Operation - Average - 210-220°F (99-104°C)

Peak - <300°F (149°C)

Table 5

Gaseous Products of Packing in Air
At Various Temperatures

<u>Temperature</u>	<u>Products</u>
>100°C	Water
120°C-130°C	Straight Chain Fluorocarbon (Surfactant)
200°C-350°C	Straight Chain Hydrocarbons, Acetaldehyde, Dimethylbutane, Methylfuran, Dimethylfuran, and Furfural
>450°C	Tetrafluoroethylene, Carbonyl- fluoride, HF (Hydrogen Fluoride) Perfluorocyclopropane
>500°C	Perfluoroisobutylene plus the above fluorinated compounds

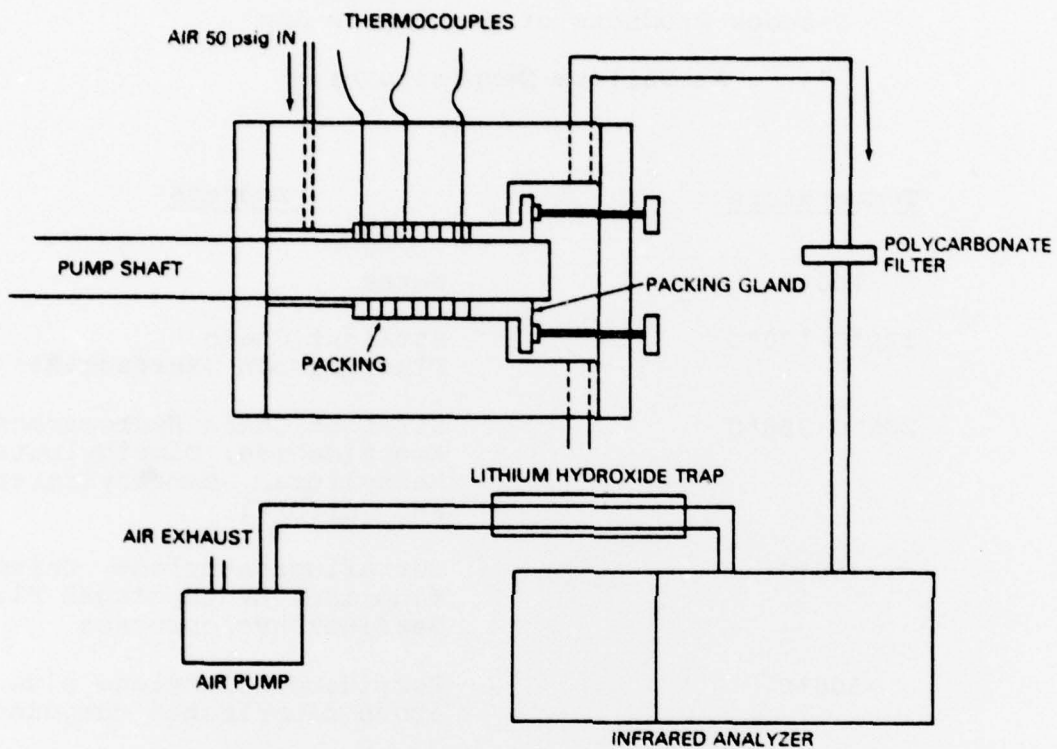


Fig. 1 - Dry operation test configuration

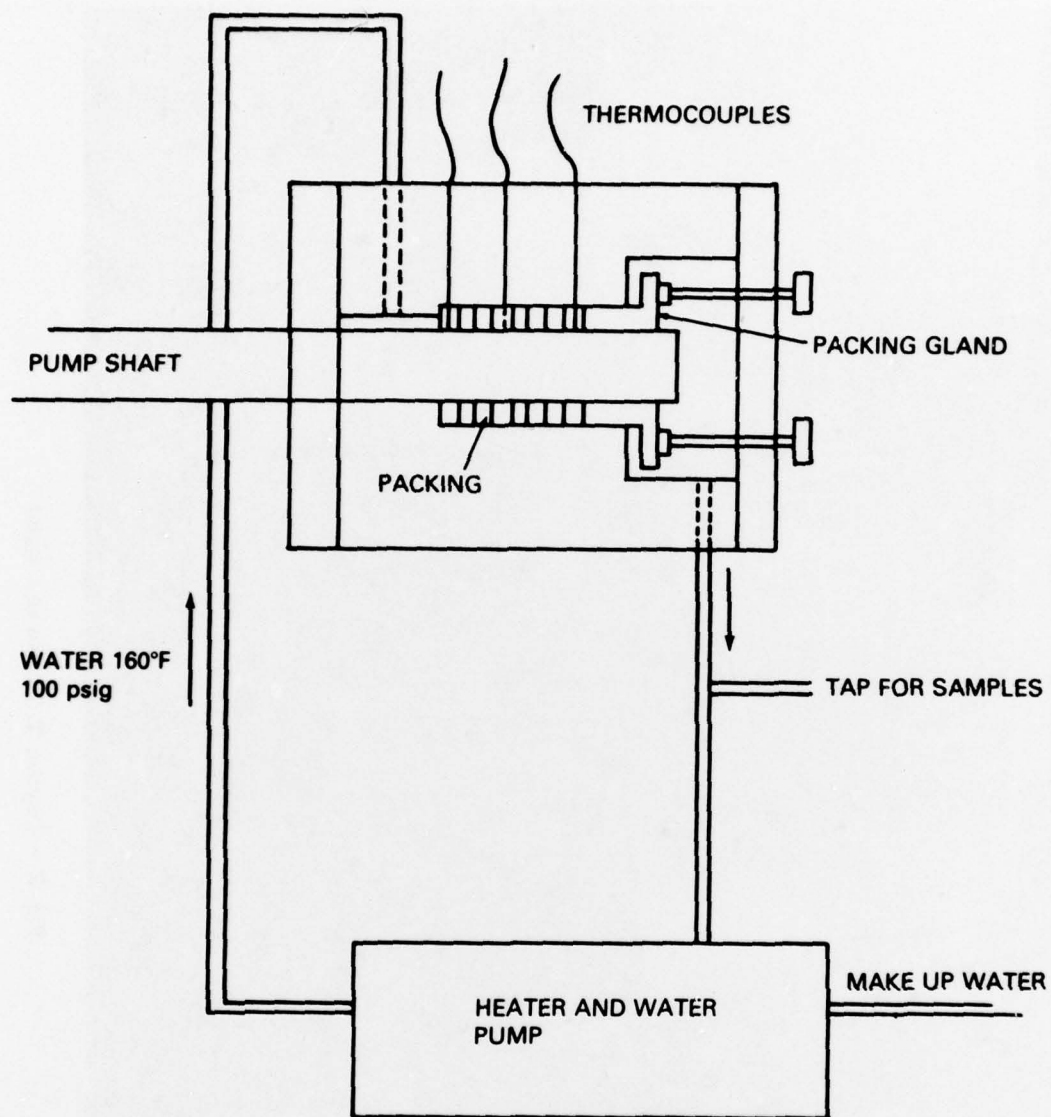


Fig. 2 - "Wet" operation test configuration

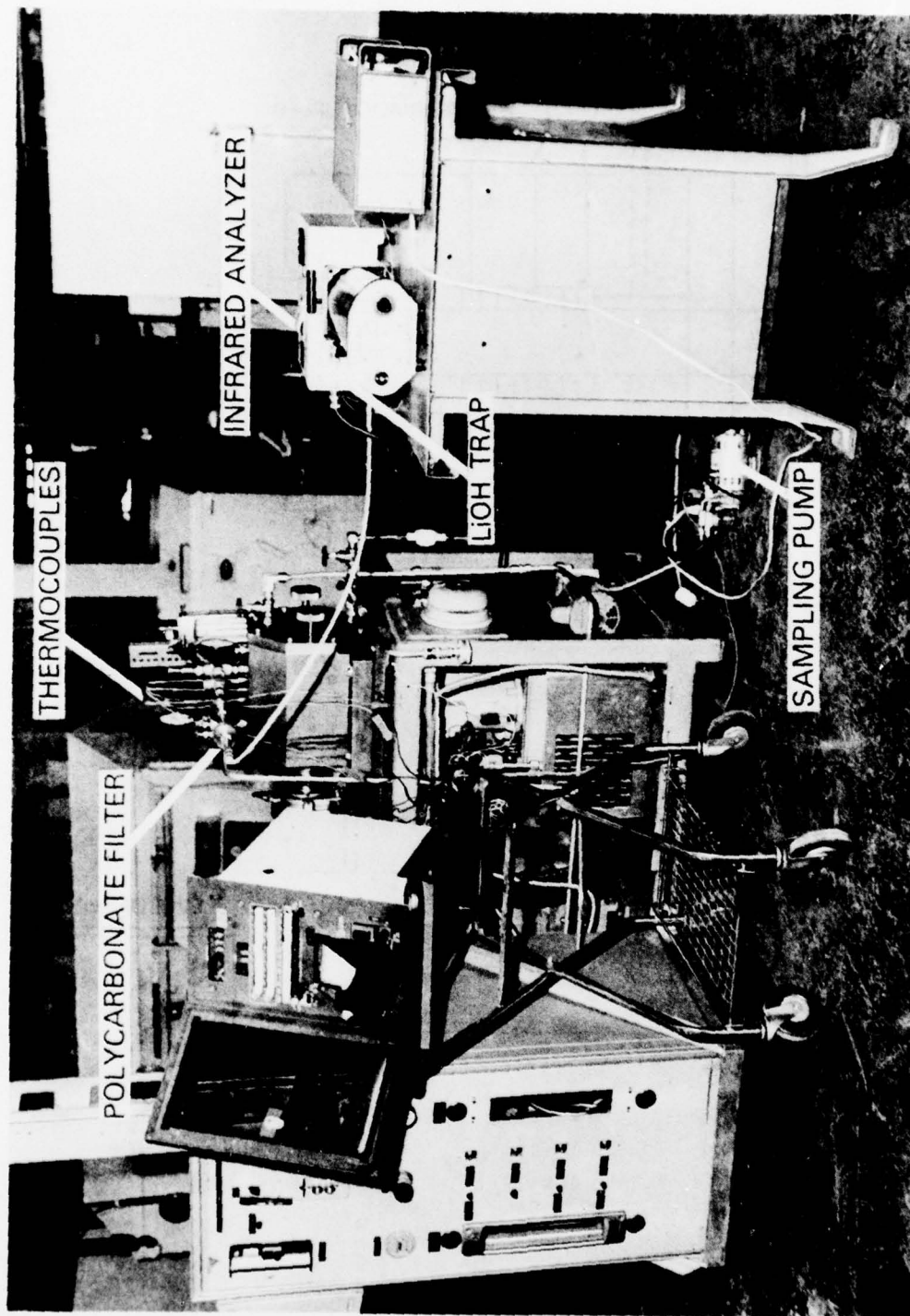


Fig. 3 — Dayton T. Brown test stand

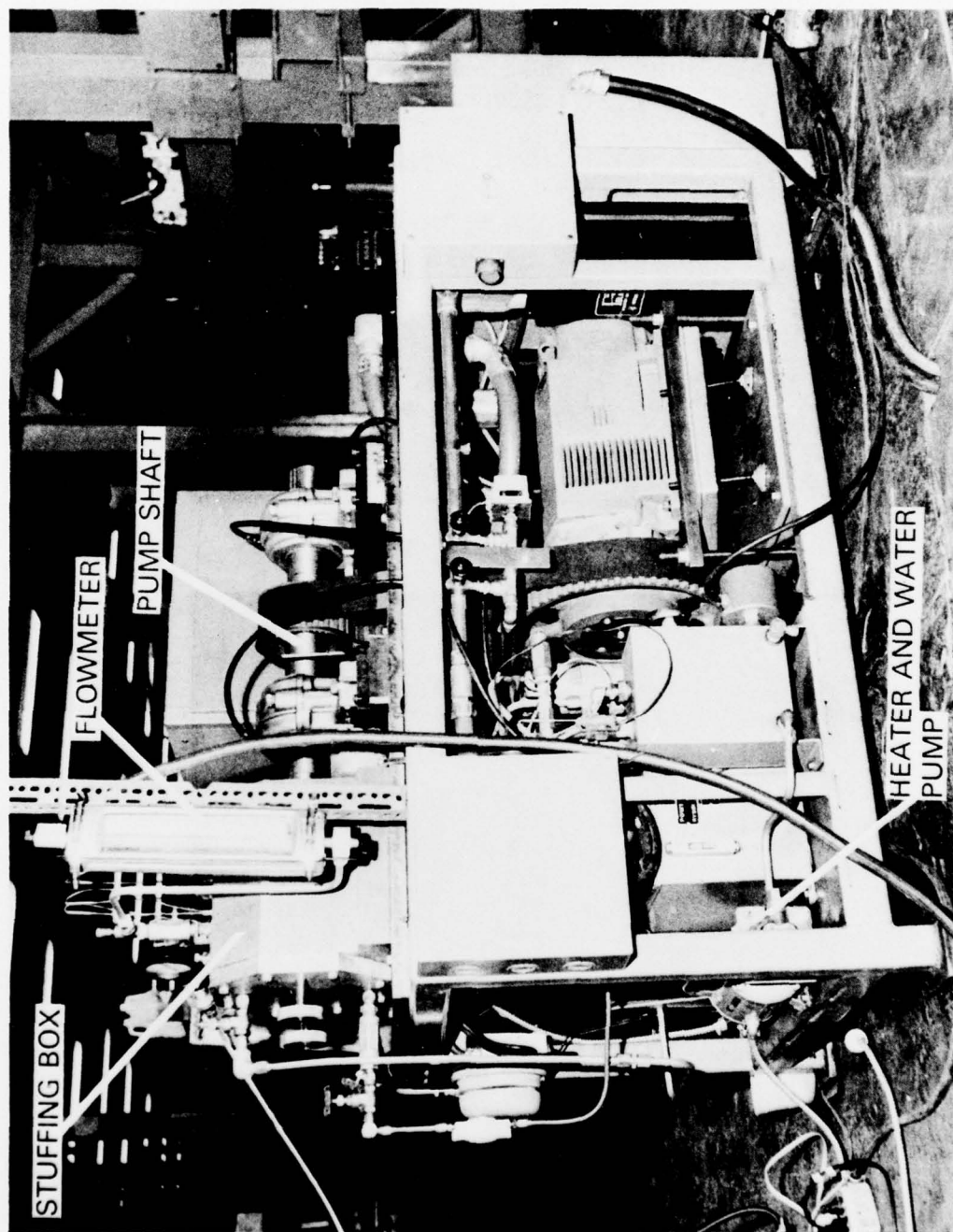


Fig. 4 — Dayton T. Brown test stand

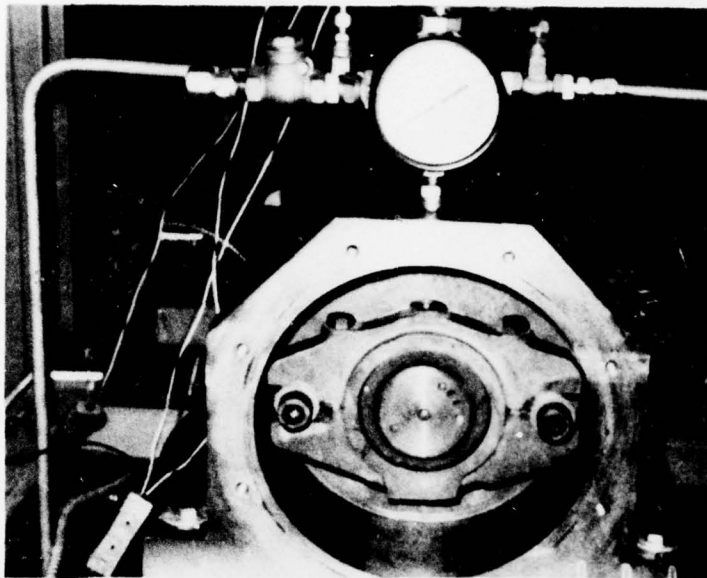


Fig. 5 — Interior of stuffing box - packing gland

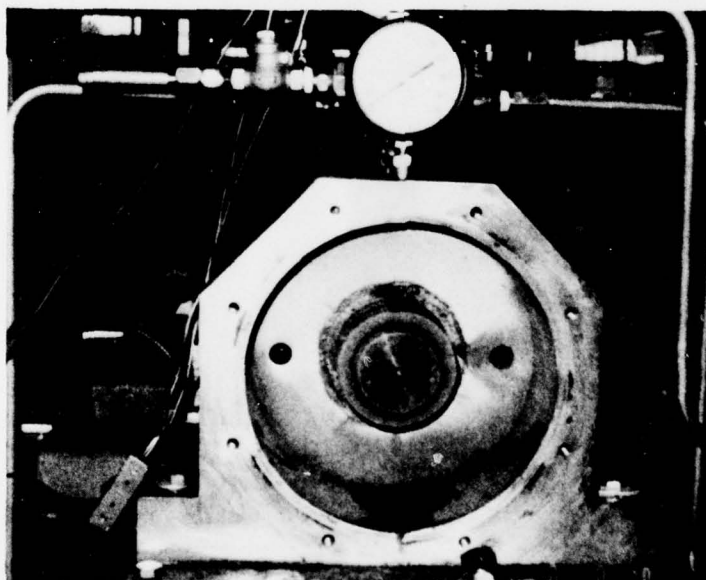


Fig. 6 — Interior of stuffing box - packing installed



Fig. 7 — Dry operation, zero leakage, 3600 RPM

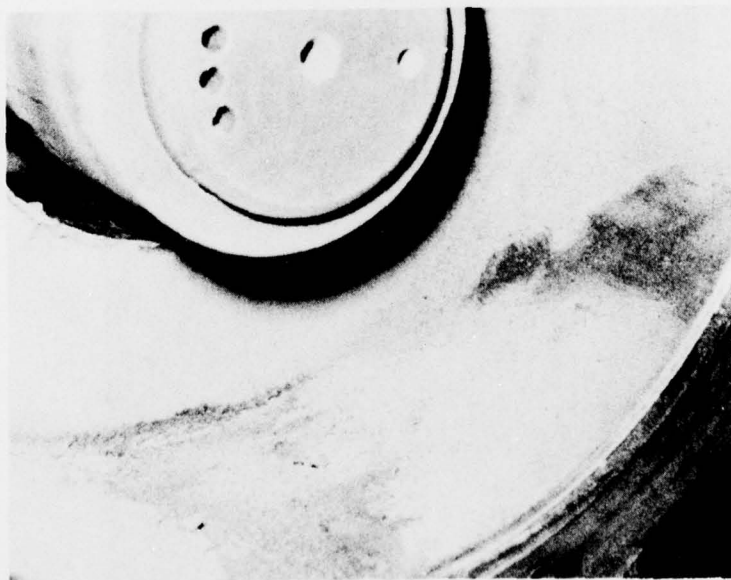


Fig. 8 — Packing residue deposited on interior of stuffing box during dry operation



Fig. 9 — Wet operation, zero leakage, 3600 RPM

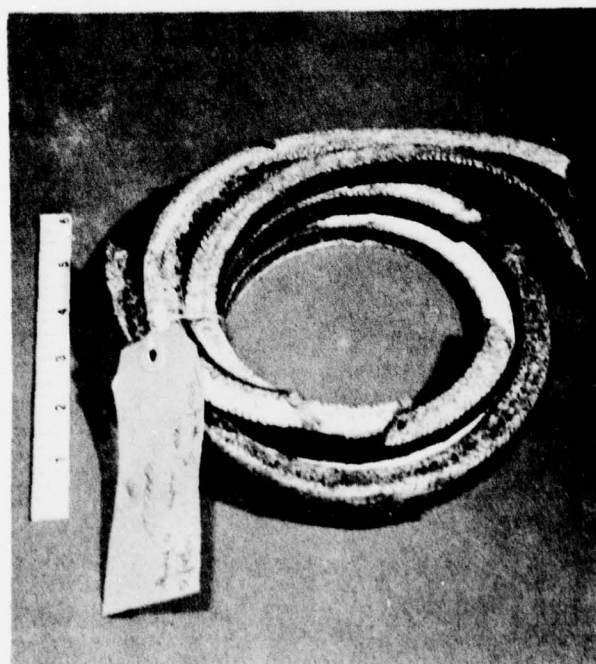


Fig. 10 — Wet operation, 8-16 drops per minute leakage, 1800 RPM

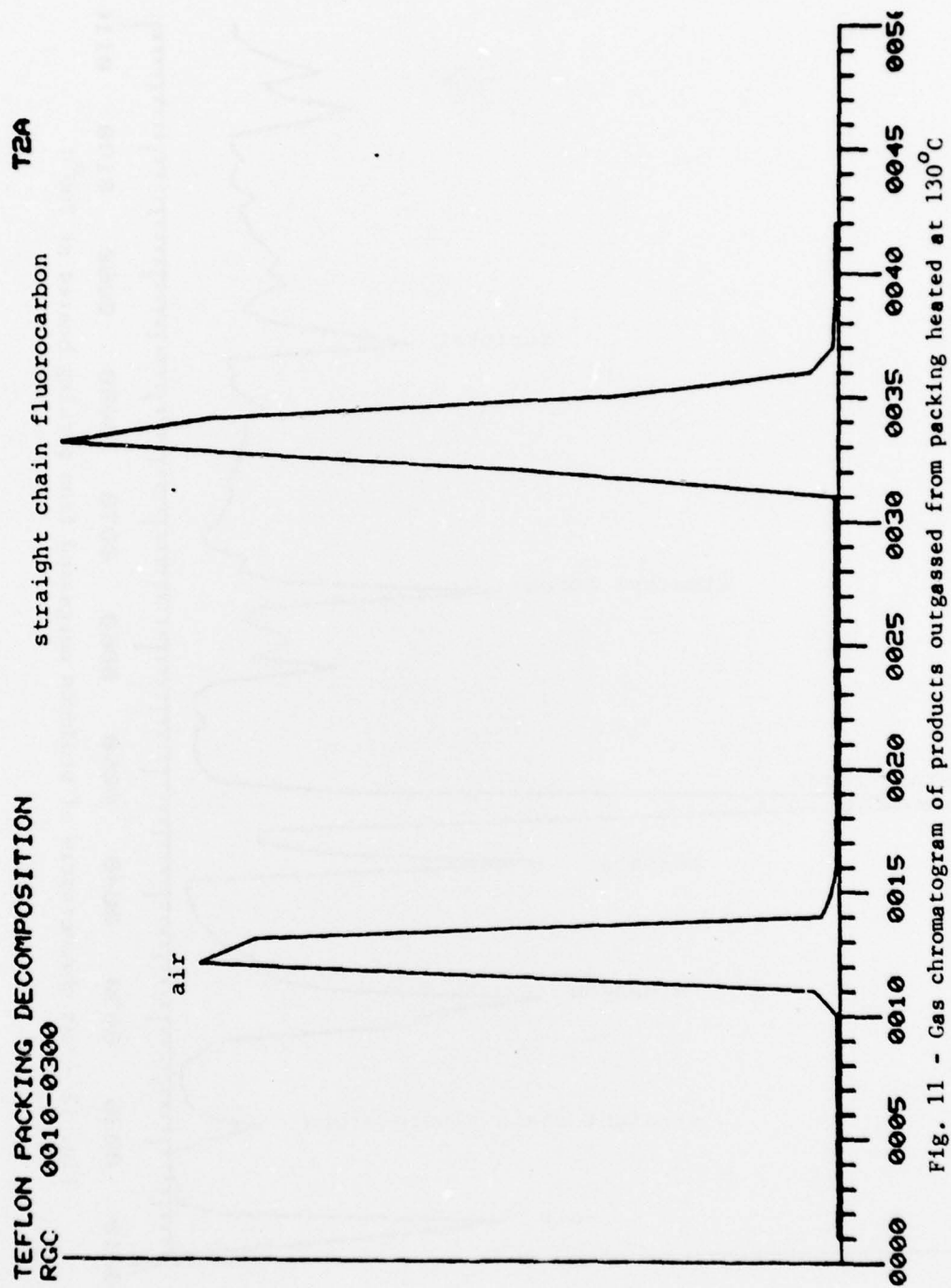


Fig. 11 - Gas chromatogram of products outgassed from packing heated at 130°C

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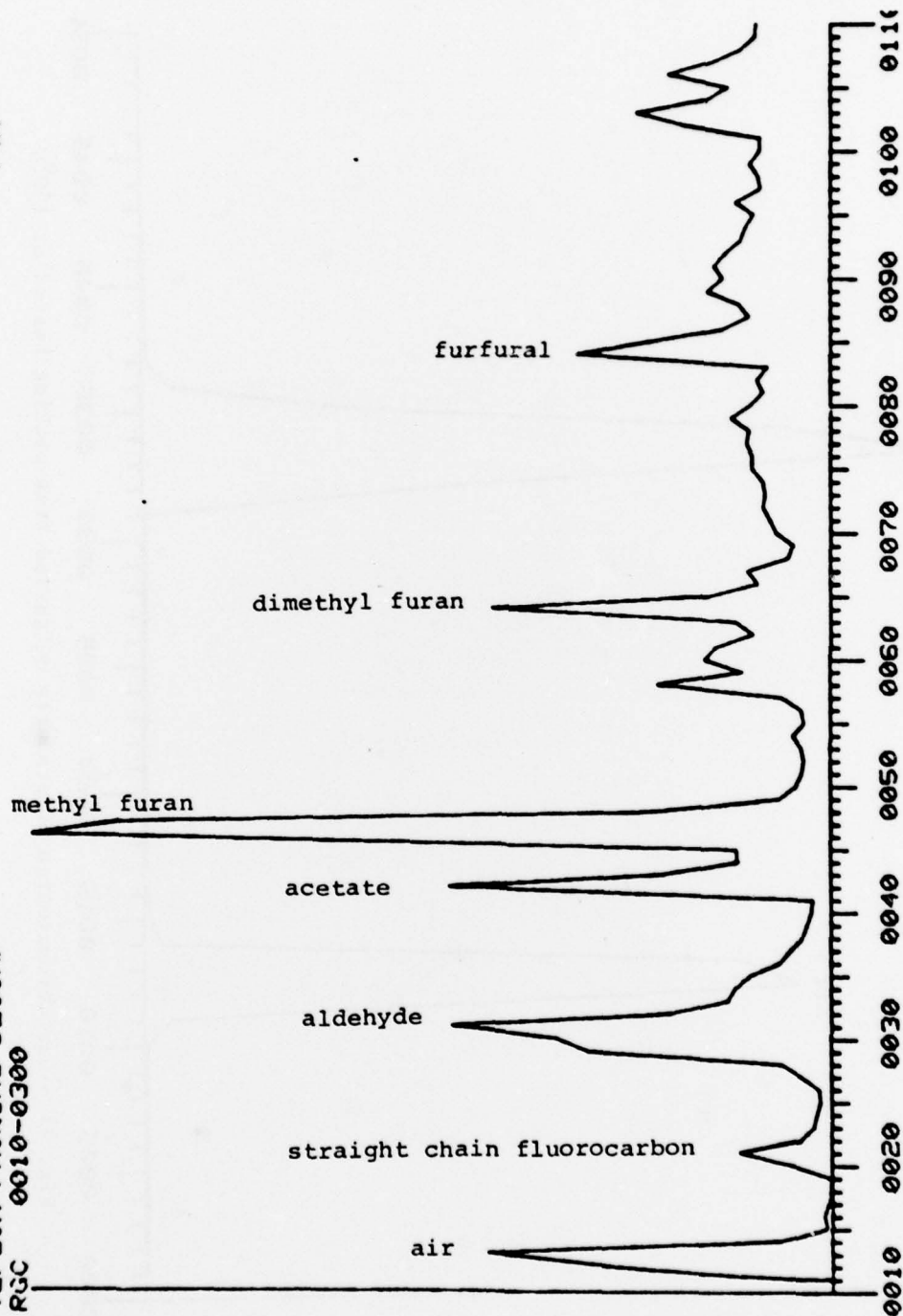


Fig. 12 - Gas chromatogram of products outgassed from packing heated at 300°C

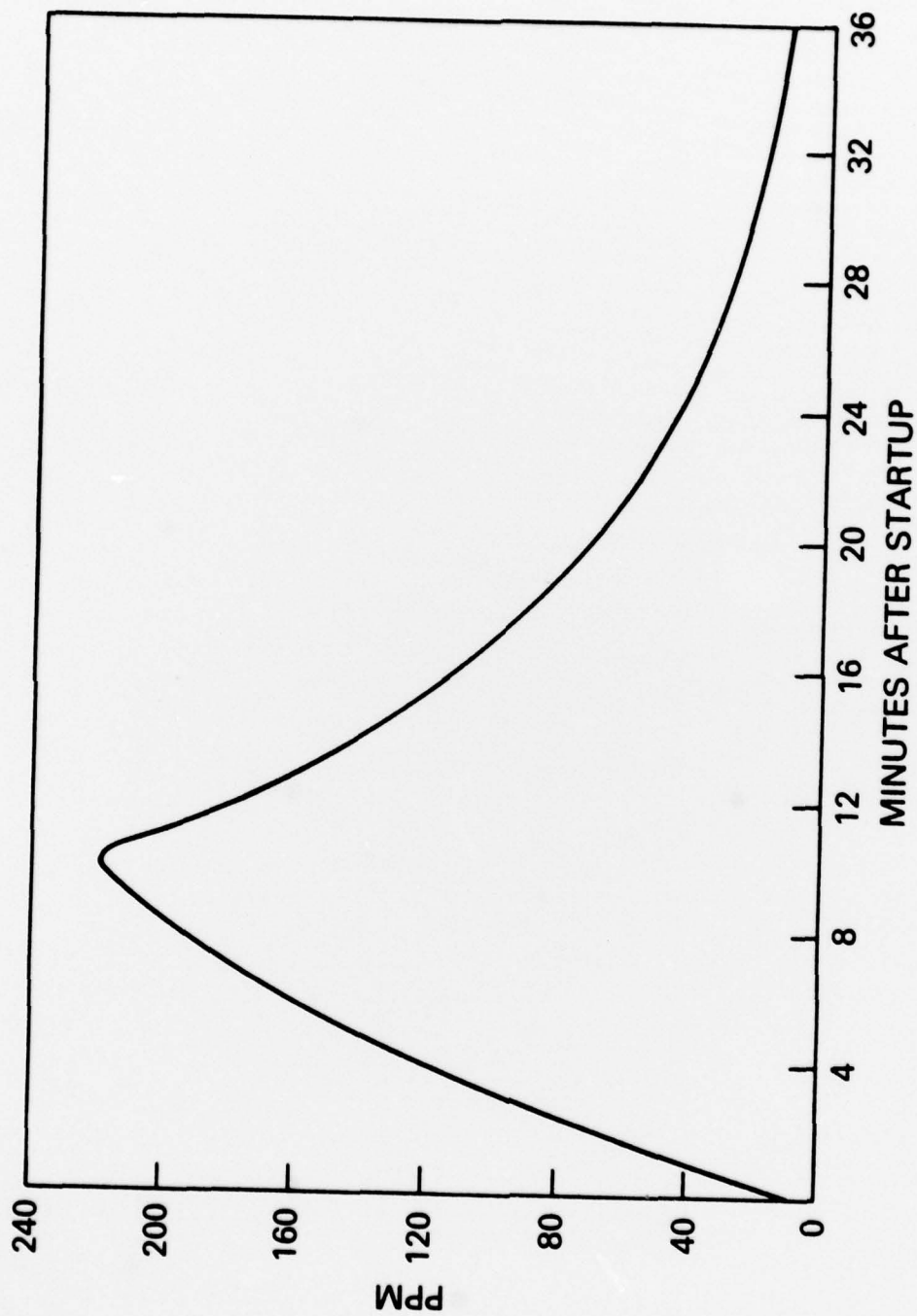


Fig. 13 - Estimated hydrocarbon concentration (based on Hexane) in the machinery space